STUDY OF ELECTROLYTIC DISSOCIATION IN STRONG ELECTROLYTES BY RAMAN EFFECT

TRICHLORACETIC ACID

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ABSTRACT The Raman spectrum of trichloracetic acid exhibits conspicuous changes on dilution of the acid. On comparing the spectra of the acid at different concentrations and of lithium and sodium salts of this acid, the lines of this acid are attributed to different kinds of radicals, $(CCl_3COOH)_2$, CCl_3COOH and CCl_3COO. This assignment is further supported by the corresponding changes that these lines undergo on increasing the temperature and the hydrogen-ion concentration by adding hydrochloric acid to this acid. Also, on comparing this acid with acetic acid, the lines are attributed to different bonds, C–C, C–O, C=O, etc.

INTRODUCTION

It is well known that trichloracetic acid is a very strong acid, comparable to nitric or hydrochloric acids in dilute solutions. But there is no evidence to show how it dissociates in concentrated solutions as the electrochemical methods, usually adopted for such studies, are applicable only to dilute solutions. But the method suggested by I. R. Rao (1930), *i.e.*, by Raman effect is best suited for such studies and has been adopted by the author for this acid also.

The Raman spectrum of trichloracetic acid has been studied by Woodward (1931), Parthasarathy (1934), Thatte and Ganesan (1931), Kohlrausch (1933), Ghosh and Kar (1931) and Cheng (1936). The studies were confined only to concentrated solutions and it was generally found that the Raman spectra were superposed by an intense continuous background. Woodward reported no apparent change in the Raman spectrum of the acid with dilution and came to the conclusion that no relation could be found between Raman effect and electrolytic dissociation of this acid from his spectra. No other systematic attempt was made to study the dissociation of the acid at various concentrations by this method. The present work is an attempt in that direction.

EXPERIMENTAL

The acid was distilled under reduced pressure by continuously drawing out the decomposition vapours and the distillate is collected direct in the Wood's tube. This is found to diminish the continuous spectrum to a large extent. With this sample, solutions of concentrations 9.0, 6.0, 3.0, and 1.5N are prepared with double distilled water. Also, solutions of CCl_3COONa and CCl_3COOLi of concentrations 3.0N each are prepared with pure substances. In order to help correct assignment of the Raman lines to various radicals, a mixture containing 1.5N of this acid with 2N HCl is also prepared.

While studying the acid at higher temperature, it was experienced that the decomposed vapours formed bubbles near the surface of the tube, which strongly diffused the direct mercury arc light. In order to avoid this, the tube is kept vertical and the scattered light is reflected, by means of a mirror set at 45°, to the slit of the spectrograph. With this arrangement, the spectra of the molten acid (at 60°C) and of 9N and 6N solutions at 80°C are taken.

RAMAN LINES

The lines and corresponding intensities are presented in the diagram. Table I gives the frequencies obtained by different authors, while Table II gives those of the author.

TABLE I

Author		Raman lines in cm^{-1}
Woodward	8.8N	190(s), 286(s), 436(s), 680(m,d), 843(m,d)
	1.6N	190(s), 286(s), 436(s), 680(m,d), 843(m,d)
Parthasarathy (solid)		250(1), 286(1), 327(1), 1538(2), 600(2)
Thatte and Ganesan		433(w), 685(st), 2091(diffuse)
Cheng		671, 700, 835, 947, 1210 (Raman lines) 14.38, 14.20, 11.06, 10.36, 8.20 (Infra red)
Kohlrausch (molten)		200(10b), 277(10b), 318(3), 433(10b), 447(10b), 676(8b), 833(5b), 946(3b), 1413(1b), 1689(0), 1713(1b)

In the above table, the numbers and letters in the brackets represent intensities of the lines, the letters having the usual significance.

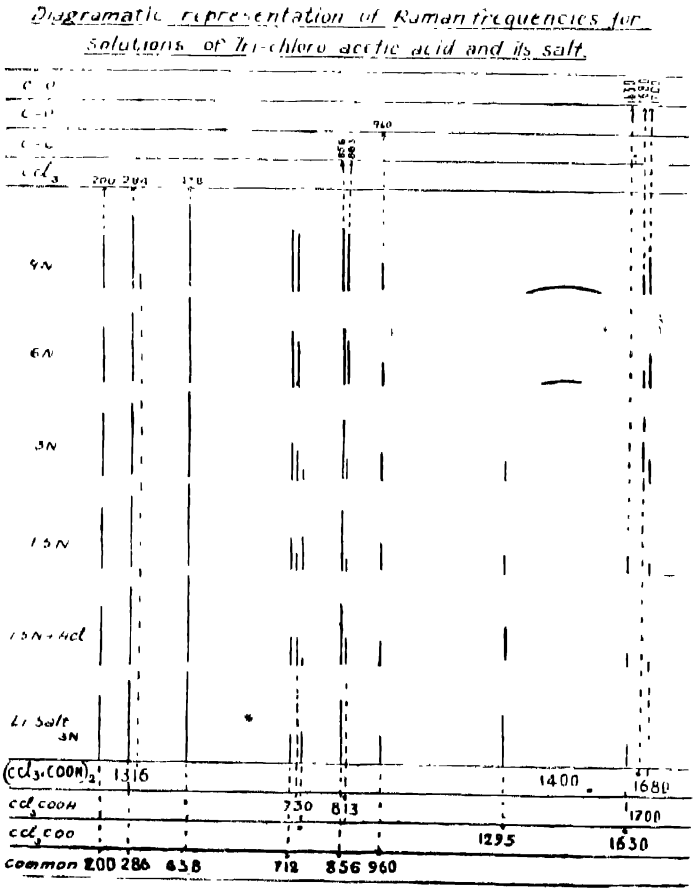
TABLE II

Molten	9.0N	9.0N 80°C	6.0N	6.0N 80°C	3.0N	1.5N	1.5N HCl	Li-salt
200(6)	200(6)	200(6)	200(6)	200(6)	200(6)	200(6)	200(6)	200(6)
284(8)	284(8)	284(8)	284(8)	284(8)	284(8)	284(8)	284(8)	284(8)
316(0)	316(0)	...	...	...	...	...	...	..
438(10)	438(10)	438(10)	438(10)	438(10)	438(10)	438(10)	438(10)	438(10)
690(4d)	712(4d)	712(4d)	712(4d)	712(4d)	712(4d)	712(4d)	712(4d)	712(4d)
...	730($3\frac{1}{2}$)	730(1)	730(3)	730($3\frac{1}{2}$)	730(2)	730(1)	730(2)	...
...	...	...	...	...	750(1)	750(2)	750(0)	750(2)
832(4d)	856(4)	856(4)	856(4)	856(4)	856(4)	856(4)	856(4)	856(4)
946(1)	960(1)	960(1)	960(1)	960(1)	960(1)	960(1)	960(1)	960(1)
...	...	...	...	...	1295(1)	1295(3)	1295(0)	1295(6)
1415($\frac{1}{2}$)	1415(0)	1415(0)	...	...	...	...	...	..
1650(d)	1680($\frac{1}{2}$)	1700($\frac{1}{2}$)	1700(0)	1700($\frac{1}{2}$)	1700(0)	1630(0)	1630(0)	1630(0

From a comparison of the Raman frequencies and the intensities of the lines obtained by various authors, it can be seen that except that of Kohlrausch all the other spectra were superposed by an intense continuous background which masked the lines. On comparing the results obtained by Kohlrausch with that of the author, it is seen that there are discrepancies in the values for the frequencies. This may be due to the fact that the lines are diffuse and exact location of the maxima is difficult.

The bands at 1089 and 1743, observed by Kohlrausch, are not found to be sufficiently resolved, nor are the two lines of frequencies 433 and 447. All the above authors, except Woodward, observed the Raman spectrum either in one concentration or in the molten acid only. Woodward studied the spectra of the acid in two solutions but could not observe the important line 1295, and thus came to the conclusion that nothing can be said from his results as regards dissociation of the acid.

In the diagram the bands 712, 730, 750 ; 850, 863 and 1630, 1680, 1700 are not as resolved as represented. Their resolution is exaggerated in order to make the assignment clear.



DIAGRAM

ASSIGNMENT OF THE LINES

The Raman spectrum of this acid is similar to that of acetic acid. Koteswaram (1938) assigned lines of frequencies 872 and 803 to C-C link, 1010 to C-O, the composite band at about 1700 to C=O, the group of lines 2880, 2940, 2996 to CH_3, in the spectrum of acetic acid. Similar considerations help assignment of lines in trichloracetic acid also to different bands. This assignment is also represented in the diagram.

From the diagram it can be clearly seen that the Raman spectrum of the acid changes with dilution, temperature and with increase of concentration of the hydrogen-ions by adding HCl. These variations can be interpreted on the basis of the changes in the dissociation of the acid.

The band 1630-1700 is found to be common to all components having the C-O band and hence can be attributed to it. In solutions of acetic acid, this band was observed by Koteswaram to be increasing in frequency on dilution and temperature. He explained that it can be regarded as composed of two components corresponding to molecules of the type $(CH_3COOH)_2$ and CH_3COOH, the lower frequency components belonging to the former. On increasing the dilution or the temperature, the lower frequency side diminishes in intensity indicating a diminution in the number of polymers which split up into monomers. Similarly, in the spectrum of the trichloracetic acid, the component 1680 which diminishes in intensity with dilution of the acid may be attributed to the $(CCl_3COOH)_2$ molecules, which, on dilution, split up into normal CCl_3COOH molecules, giving rise to the component at 1700. The rapid diminution of the intensities of the Raman lines 316 and 1400 also can be explained on the above basis.

The bands 712-750, 856-803 and 1630-1700 can be regarded as composed of a number of components as shown in the diagram. The components 730, 863 and 1700 diminish in intensity on dilution and are absent in the salt solution. This can be explained if they are attributed to the normal CCl_3COOH molecules, which dissociate into ions on dilution. The brightening up of these lines in the HCl mixture, from suppression of dissociation, may be expected to support the above view.

The components 730, 1295 and 1630 are absent in concentrated solution of the acid, but first make their appearance in the spectrum of the 3N solution. With dilution they become more intense and are brightest in that of the salt solution. Those lines can be regarded as characteristic of the CCl_3COO' ions. The absence of this line in the HCl-mixture corresponding to the suppression of dissociation also is in support of the above view.

The other lines 200, 284, 438, 712, 856 and 960 are found in all these solutions and can, therefore, be regarded as common to all the three types of radicals, $(CCl_3COOH)_2$, CCl_3COOH and CCl_3COO'. The gradual diminution of the line 712 with dilution suggests that its specific intensity corresponding to the ions is less than that for the normal molecules.

The above assignment of the lines to various radicals and bonds is clearly demonstrated in the diagram.

TEMPERATURE EFFECT

On comparing the intensities of the components 712, 730, 1700, for the concentrations 9N and 6N at 30°C and 80°C, the following points can be noticed. At higher temperature,

1. The component at 730 increased in intensity, indicating an increase in the number of normal CCl_3COOH molecules.

2. The C=O band at 1680 shifts to higher frequency (1700), indicating a diminution in the number of polymers.

Therefore, it should be stated that just as in the case of other associated molecules like acetic acid, this acid also exhibits depolymerisation with temperature.

HYDROGEN-ION EFFECT

In a previous communication by the author (Rao, N. R., 1942), it was reported that if in a solution of a strong acid the concentration of the H ions is increased, the dissociation of the acid will be strongly suppressed. This point is tested in the case of this acid also. In the diagram, it can be seen clearly that the intensity of the lines corresponding to the ions are strongly suppressed in the mixture with HCl, compared to the pure solution of the same concentration (1.5N) This is a further proof of the correctness of the assignment of the lines to different radicals.

DISCUSSION

The above changes in the lines of the acid with dilution show clear evidence for the dissociation of the acid. A quantitative investigation of the degree of dissociation is not possible for the following reasons. On exposure to the incident radiation, the solutions develop, owing perhaps to photochemical decomposition, a slight violet colour, which is different for different concentrations. Hence, they absorb light to different extents. On account of the fact that this colour increases with time, it was not possible to determine the actual absorption, with a view to eliminating its effect on the relative intensities of the lines. The continuous background is also found to increase on dilution.

But a rough estimate of the dissociation in 1.5N solution of the acid is made by comparing the intensity of the line 1295, corresponding to the CCl_3COO' ions in these solutions with that in the salt solution. Such a comparison shows that the degree of dissociation in 1.5N solution is only 60%, while the corresponding value for nitric acid is about 95%. Hence, it should be concluded that this acid

is much weaker than nitric acid in concentrated solutions. In dilute solutions, the two acids are of the same strength, as revealed by conductivity data.

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REFERENCES

Cheng, 1930, *Ann. Phys.* (11) **5**, 427.
Ghosh and Kar, 1931, *J. Phys. Chem.*, **35**, 1735.
Kohlrausch, 1933, *Z. f. Physik. Chem.*, **21B**, 342.
Koteswaram, 1938, *Zeit. f. Phys.*, **110**, 118.
Parthasarathy, S., 1934, *Phil. Mag.* (suppl.), **77**, 471.
Rao, I. R., 1930, *Proc. Roy. Soc.* (Amsterdam), **127**
" " (London), **33**, 632.
Rao, N. R., 1942, *Current Science*, **1**, 15.
Thatte and Ganesan, 1931, *Phil. Mag.*, **12**, 825.
Woodward, L., 1931, *Physik. Z.*, **32**, 774.